

Characterization of Optical and Associated Properties of Marine Colored Dissolved Organic Material (CDOM)

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LONG-TERM GOALS

Our long-term goal is to understand the factors affecting the optical characteristics of seawater. Our focus is on developing an understanding of the physical and chemical processes affecting colored dissolved organic material (CDOM), and the resultant attenuation changes in ultraviolet and visible radiation in seawater and coastal environments. The chemical constituent of seawater that absorbs most of the incident solar radiation is collectively referred to as CDOM. CDOM is a complex aggregate of various organic compounds derived from marine biota and terrestrial humic material introduced to the oceans by rivers. The photochemically active fraction of these materials initiates most of the photochemical reactions in seawater, altering CDOM itself and initiating chain reactions that affect the chemical speciation of oxygen, transition metals and various organic compounds. These reactions can have profound effects on the chemical characteristics of seawater and physical properties such as optical absorbance and luminescence. Our primary goal is to understand the differences and similarities between DOM of marine and terrestrial origin, and the impact these properties have on the chemical and optical characteristics of coastal environments.

OBJECTIVES

To develop models for the detailed optical and chemical characterization of CDOM, we must understand both its physical nature and the chromophores composing the DOM matrix. This requires the application of powerful new techniques not previously used in the study of marine DOM. Our objective is to determine the feasibility of coupling Flow Field Flow Fractionation (FFFF) as the separation technique together with optical characterization of fractionated CDOM by absorbance and fluorescence techniques and structural characterization by LC/MSⁿ. Our principal focus over the last year was to complete the installation and testing of our newly purchased FFFF system (ONR DURIP/1997: "Characterization of Coastal Optical Properties Through the Application of Flow Field Fractionation") and to evaluate two potential detection methods (LC/MSⁿ and fluorescence lifetimes).

APPROACH

Our approach over the last year has combined exploring the capabilities of the FFFF system extensively in the laboratory, with submitting test samples of DOM to manufacturers of potential detectors for evaluation on their instruments. We also sampled natural waters in South Florida to

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provide a series of riverine and marine DOM samples for the purposes of method development and evaluation.

WORK COMPLETED

To test the FFFF system and proposed detection methods, we acquired natural water samples of DOM. As our primary goal is to understand the similarities and differences between DOM of marine and terrestrial origin and their impact on optical characteristics of coastal environments, we used a series of fifteen samples from a Southwestern Florida riverine to marine transition zone. Samples were taken from the Shark River, which receives significant organic input from the Everglades and discharges into the Gulf of Mexico. Samples were also taken in Florida Bay following the river plume, representing a time series. As preliminary characterization of the samples, we measured the salinity, absorbance, total organic carbon (TOC) and DOM fluorescence (vs. quinine sulfate).

The technique of Flow Field Flow Fractionation (FFFF) has been used to characterize soil and riverine humic substances (Beckett et al., 1987). Separation in FFFF relies on molecular diffusion coefficients i.e. molecular size. FFFF thus has many advantages compared to other common techniques of DOM fractionation that suffer from charge adsorption and charge repulsive effects. In preliminary work, we showed FFFF could be applied to DOM samples from riverine, coastal and oceanic regions (R.G. Zika and D.D. Riemer, unpublished work, 1996). An FFFF system was purchased for our laboratory in 1997 with ONR DURIP funds. A first-year graduate student, Eliete Zanardi, has done most of the FFFF system setup and evaluation. This work will be incorporated into her Ph.D. research dissertation.

Initial progress was slow due to operational software/hardware difficulties, but these were resolved in the first half of this year. The FFFF system was run under a wide variety of conditions, using both humic standard materials and natural samples, to derive optimal operating parameters for DOM fractionation. These were successfully determined by running an Aldrich humic standard material on the FFFF system under a variety of flow conditions. The effect of an added buffer solution in the carrier fluids has also been evaluated (Beckett et al., 1989). To examine the effect of solution matrix on sample fractionation, a series of Aldrich humic standard samples were run. These samples had been prepared with the same concentration of the humic substance but with varying amounts of sodium chloride and hence different salinities. The reproducibility of the measurements and robustness of the column were extensively examined with these standard solutions. Bulk Shark River water samples have also been run and compared to the standard Aldrich humic materials under the same conditions (salinities, flow rates, concentrations). FFFF fractograms for Shark River low salinity samples showed a broad peak, with a second broad peak as a shoulder. The same results were found for the Aldrich standard humic substance at the same salinities. More saline solutions showed a reduced first peak and larger second peak, with increased separation between the two, indicating an effect of the solution medium on the apparent size of the humics. Now that we have established optimum operating conditions for DOM, experiments are underway to size-calibrate the FFFF system by running commercial standards of known molecular sizes.

Following separation, a variety of techniques may be used to detect the size-fractionated components in the FFFF eluent. All preliminary experiments were performed with an in-line HP 1100 series diode array UV-VIS detector, with absorbance measured in the range 200 – 700 nm. We are awaiting delivery of an in-line HP 1100 series excitation-emission diode array fluorescence detector, which will greatly enhance our DOM analytical capabilities by increasing our sensitivity and specificity. We also

evaluated two additional detector modes that have not, as far as we know, previously been applied to the detection of chromatographically separated DOM components, namely LC/MSⁿ for structural characterization and time resolved fluorescence spectroscopy for fluorophore characterization via lifetimes. The limited previous lifetime studies on composite DOM samples have indicated that multiple lifetimes in the range of 50 picoseconds to 10 nanoseconds exist, with several fluorophores present (Milne et al., 1987; Jones and Indig, 1996; Hemmingsen and McGown, 1997). Fluorescence lifetimes can be more specific than bulk fluorescence intensity measurements in identifying fluorophores and more sensitive to molecular structural changes. With LC/MSⁿ, complex molecules in the liquid FFFF eluent can be fragmented in the mass spectrometer, with the resulting fragments repeatedly isolated and re-fragmented to yield compositional information that is difficult to obtain by other means. By applying this technology to DOM, we can look for structural differences and similarities between chromatographic fractions of DOM and correlations between the structural information and optical characteristics.

Samples of Shark River and off-shore DOM extracts were sent to both Hewlett-Packard/Bruker and Finnigan-ThermoQuest for evaluation on their commercial LC/MSⁿ systems. The same test samples were sent to PTI for measurements on their commercial LaserStrobe fluorescence lifetime spectrometer. Initial results indicated both methods are very promising for characterization of DOM. The balance of the DURIP funds will be used to purchase a detector for the FFFF system. However, as we have sufficient funds to purchase only one, we will acquire the LC/MSⁿ system. We are in the process of ordering an instrument from Hewlett-Packard/Bruker, and expect to take delivery in early 1999. To continue with the fluorescence lifetime measurements, we have initiated a collaboration with Guilford Jones, Professor of Chemistry in the Photonics Center at Boston University. Dr. Jones has previously examined fluorescence lifetimes of standard humic acids (Jones and Indig, 1996) and has a PTI LaserStrobe fluorescence lifetime spectrometer in his laboratory. Initial measurements on bulk samples from the Shark River have been completed, and experiments on fractionated DOM and ultrafiltration concentrates of the whole sample series are underway.

RESULTS

Our new experimental approach to DOM studies couples FFFF as the separation technique with structural characterization by LC/MSⁿ and fluorophore identification via fluorescence lifetimes. Preliminary results indicate these techniques have strong potential capability for CDOM structural and optical characterization. Results to date also show structural and optical differences between CDOM in fresh and coastal South Florida waters that require further investigation.

To the best of our knowledge, we are the first to apply FFFF to characterize a series of riverine and coastal DOM samples. We have successfully completed the installation of our FFFF system and identified optimal operating parameters for DOM fractionation, as well as decided on LC/MSⁿ as the optimum chromatographic detector. These were our primary objectives for the last year. Initial evaluation studies with LC/MSⁿ analyses of Shark River headwaters and Florida Bay extracts showed that the marine and freshwater samples have different structural components. The absorbance of fractions eluting off an HPLC column, together with the molecular ion intensities of the fractions, also indicated that the optically active species generally constitute a small amount of the total CDOM mass. This is the first application of LC/MSⁿ to the study of DOM (Vincenti, 1997).

Fluorescence lifetime studies on the South Florida DOM water samples indicate that several fluorophores are present, with multiple lifetimes in the range of 0.8 to 7 nanoseconds. The more

marine samples have shorter lifetimes and generally blue-shifted excitation/emission wavelengths compared to the freshwater samples, possibly indicative of phototransformation/photodegradation. These measurements constitute the first fluorescence lifetime measurements for DOM in a riverine to marine transition zone. The results of this work will be presented at the following meeting, in a special session on “Composition and Reactivity of DOC: Comparisons Across Freshwater and Marine Environments”:

E. Zanardi, C. Moore, C.D. Clark, J. Jimenez, G. Jones and R.G. Zika, “Fluorescence Lifetimes of Size-fractionated CDOM in a South Florida Riverine to Marine Transition Zone”, ASLO Meeting, Santa Fe, February 1999.

IMPACT/APPLICATIONS

Aside from developing an understanding of the factors affecting the chemistry and physics of light in the ocean, there are other more applied potential future impacts. The most important of these is the development of new analytical system approaches for elucidating the structural and optical characteristics of complex organic substances in the environment.

TRANSITIONS

Our results suggest that coupling FFFF as the separation technique, with structural characterization by LC/MSⁿ and fluorophore identification via fluorescence lifetimes, is a promising route to elucidating the behavior of CDOM and potentially other complex organic substances in marine systems. We have begun a collaboration with Dr. Gil Jones (Boston University) to perform lifetime measurements on fractionated CDOM. In general, we see a strong future for the transition of the FFFF and LC/MSⁿ instrumentation/techniques to the study of other complex organic systems (eg. volatile organic carbons and polycyclic aromatic hydrocarbons in aerosols), both in this laboratory and elsewhere.

RELATED PROJECTS

A thorough understanding of the nature of CDOM in the oceans requires a multi-disciplinary approach, incorporating optical physics and marine biology in addition to marine chemistry. In related ONR and EPA sponsored work, we are developing remote autonomous sensor packages for use in coastal surveillance applications and examining the effects of ultraviolet-B radiation on marine phytoplankton species.

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